



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US86/01611 <b>(22) International Filing Date:</b> 7 August 1986 (07.08.86)  <b>(31) Priority Application Numbers:</b> 763,961 773,861 773,830 773,862 797,670 807,738  <b>(32) Priority Dates:</b> 9 August 1985 (09.08.85) 9 September 1985 (09.09.85) 9 September 1985 (09.09.85) 9 September 1985 (09.09.85) 13 November 1985 (13.11.85) 11 December 1985 (11.12.85)  <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> UNION CARBIDE CORPORATION [US/ US]; 39 Old Ridgebury Road, Danbury, CT 06817 (US).	<b>(72) Inventors:</b> HOY, Kenneth, Look ; 839 Mac Queen Boulevard, St. Albans, WV 25177 (US). RICHEY, Forrest, Alden, Jr. ; Route 6, Box 138, Charleston, WV 25311 ( ).  <b>(74) Agent:</b> FINNEGAN, Reginald, J.; Union Carbide Corporation, Law Department - E134, 39 Old Rid- gebury Road, Danbury, CT 06817 (US).  <b>(81) Designated States:</b> AT (European patent), BE (Euro- pean patent), CH (European patent), DE (European patent), FR (European patent), GB (European pa- tent), IT (European patent), JP, LU (European pa- tent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> CARBAMATE COATING COMPOSITIONS  <b>(57) Abstract</b>  High solids coating compositions are made by blending a crosslinkable organic polymer, and organic solvent and/or diluent, at least one reactive carbamate derivative, a crosslinking agent and optionally a crosslinking catalyst. The result- ant high solids coating compositions can be either solutions or dispersions depending upon the particular polymer and sol- vent and the reactive carbamate chosen as the reactive cosolvent or reactive diluent.		

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CARBAMATE COATING COMPOSITIONSField of the Invention

This invention pertains to the preparation of high solids coating compositions and more particularly to the use of nearly non-volatile substituted carbamates as reactive diluents and reactive cosolvents together with an organic volatile solvent to form the liquid vehicle for the application of film forming polymers. High solids coatings for the purpose of the present invention shall mean organic coating compositions in which the organic volatile solvents of the coating are minimized by the substitution of a reactive diluent and/or a reactive solvent for all or a part of the volatile solvent or diluent usually employed to make useful coating compositions from a particular film forming polymer. The coating composition may be of two types: (1) stable dispersions of an organic polymer in an organic diluent (so called NAD or organosol), (2) solutions of organic polymers in organic solvents. It is the intent of this invention to disclose the preparation of high solids coating compositions which utilize at least one organic, non-volatile substituted, reactive carbamate which is also a solvent or dispersant for a film forming polymer to replace a part or all of the thinner required to reduce the coatings formulation to the required applications viscosity.

Background of the Invention

The use of volatile organic solvents or diluents to dissolve or disperse high polymers in

- 2 -

the formulation of organic polymer compositions and their subsequent application onto various substrates requires the handling and disposal of large volumes of organic materials. Because of the environmental objections to solvent emissions and the increasingly frequent discovery of latent health problems of persons exposed to certain solvent vapors, alternative methods of coatings application become a necessity. Consequently there is a renewed interest in coatings technologies which can minimize the emission of Volatile Organic Compounds (VOC). One of the most promising technologies for the reduction of solvent emissions is high solids coatings. In this technology the technical approaches have been: (1) to increase the amount of polymer which can be dissolved and applied by a given amount of solvent by lowering the molecular weight of the polymer and (2) to prepare a stable dispersion of a high polymer in a volatile organic diluent.

In the first approach (solution), lowering the molecular weight of the polymer has serious consequences on the end-use performance of the coating. These problems have been compensated for by incorporating reactive functionality along the backbone and/or at termination of the polymer molecule, and after application converting these relatively low molecular weight polymers to high polymers through coupling and/or crosslinking reactions. Even with the advent of highly specialized reactive polymer systems, there is a limit as to how much molecular weight can be lowered to attain higher solids. Beyond this limit the

- 3 -

polymers are no longer film forming, have poor application properties and in general do not provide acceptable coating compositions.

The second approach (stable dispersion), is not without its adverse consequences also. While it is true that dispersions have much lower viscosities at much higher solids concentrations, other problems arise. Because of the physical constraints of particulate packing, pigmentation becomes difficult and film formation becomes a sintering process. Most often, in these systems, there is the need of fugitive plasticizers to insure the continuity of the film. Even then gloss, film smoothness, hardness, adhesion, pigmentation and ultimate performance can be adversely affected.

To address these newer problems imposed by adoption of either of these high solids technologies, coatings technologists have incorporated reactive solvents and/or reactive diluents into coatings formulations. Reactive solvents and reactive diluents as used herein are nearly non-volatile organic materials which have as an integral part of their structure a plurality of functional groups which are co-reactive with the base film forming polymer and/or required crosslinking agents, and can replace a part or all of the volatile organic solvent and/or diluent required to reduce the formulation to a reasonable application viscosity. They may be liquids or solids providing, those which are solids are soluble, fusible, and compatible with the film

- 4 -

forming components either before or after application and subsequent cure.

Adoption of this definition imposes some requirements on materials which can be considered as reactive solvents and reactive diluents. They must be: - (1) essentially non-volatile under the conditions required for cure of the coating, (2) good solvents for the film forming polymers or in the case of the dispersions, be temporary plasticizers for the base polymer during film formation, (3) latently co-reactive with the film forming polymer and/or the cross-linking agents under conditions required for polymer conversion, and finally (4) be able to provide final film properties required for the intended application. Because reactive diluents and reactive solvents do become a considerable part of the final film, the properties of the coating are related not only to the properties of the film forming polymer but also to the properties attained from the reactive solvent or reactive diluent upon chemical incorporation into the composition. Often it is necessary to adjust the structure of the film forming polymer to compliment the structure of the reactive diluent. Such polymers are designed for this intended use, and are preferable to polymers used in much of the prior art. However, even polymers of the prior art can be formulated, using reactive diluents and/or solvents, into coating compositions with lower emissions than the corresponding formulation of these identical polymers using only volatile non-reactive solvents and/or diluents.

- 5 -

The advantages of high solids coatings can be illustrated by the use of compositional phase diagrams. Since the teachings of the present invention may be applicable to coatings of either the dispersion type or solution type, two compositional phase diagrams will be required to understand the phase relationships. Figure 1 is a simplified phase diagram of a hypothetical dispersion high solids coatings system, representing the volatile diluent as A, the reactive diluent as C, and the film forming polymer including the cross-linking agent as B. The area of a single phase, 2, is separated from the area of two phases, 4, by the curved line A-A'-B. The point E represents the application composition of the high solids dispersion coating. The straight line E-D represents the changing compositions during film formation; the dashed line E-B is the film forming pathway that the high solids coating of the prior art would take. In the later case the diluent C' is the fugitive plasticizer required for particle coalescence and must be removed from the film by vaporization otherwise performance properties would be degraded. In the former the reactive diluent remains an internal part of the film and is incorporated into the polymeric film by reacting with the polymer through the reactive functionalities provided. The salient features of the phase diagram are: (i) the reactive diluent is compatible with (soluble in) the base film forming polymer; (ii) the reactive diluent serves as a transient plasticizer to allow film coalescence;

- 6 -

(iii) the reactive diluent need not be totally soluble in the volatile diluent, but rather is initially distributed between the organic liquid phase and the polymer phase and during evaporation of the volatile diluent is translocated totally to the polymer phase; (iv) because the reactive diluent is essentially non-volatile and becomes a part of the final coating, the total non-volatiles (total solids) of the coating is equal to the sum of the polymer including the cross-linker and the reactive diluent thus allowing lower volatile organic emissions.

Figure 2 is a simplified compositional phase diagram of a hypothetical high solids solution coating composition representing A, as the volatile organic solvent, the reactive solvent as C, and the film forming polymer including any required cross-linking agent as B. Because of economic constraints the volatile organic solvent, often lower cost hydrocarbons, alone is generally not a good solvent for the film forming polymer, and thus the area of a single phase, 2, is separated from the area of two phases, 4, by the curved line A-A'-B. The point E represents the applications composition of the high solids solution coating. The straight line E-D represents the changing compositions during the film forming process. The dashed line E-B represents the film forming pathway of a corresponding solution coating when C is a volatile organic solvent. The notable features of Figure 2 are: (i) The reactive solvent is generally miscible with the volatile organic solvent; the line A-C is



- 7 -

in the one phase region in its entirety. (ii) The coatings polymer is soluble in the reactive solvent; the line C-B is in the one phase region in its entirety. (iii) The reactive solvent is essentially non-volatile and becomes a part of the final coating and consequently, the total solids (non-volatiles) in the film, point D, is equal to the sum of the polymer including any required cross-linker and the reactive solvent.

In both cases the reactive diluent and/or reactive solvent becomes a part of the final coating and as such must contribute to, and not detract from the overall coating performance. The reaction product of polymer, reactive diluent and/or reactive solvent and the cross-linking agent must have suitable properties such as toughness, adhesion, impact resistance, abrasion resistance, scratch resistance, resistance to solvents, chemicals, acids, and bases. It must have good color, gloss, and stability as is required according to the end use application. All of the above is well understood by those skilled in the art.

Initially the coatings technologist adapted materials which were readily available for use as reactive solvents and reactive diluents. Many of these materials have limited utility because of excessive volatility, limited reactivity, poor compatibility with the base film forming system, and in general degradation of overall coatings performance. Typical of the early reactive solvents and diluents are higher boiling polyols e.g., glycerol, monoglycerides of unsaturated fatty acids,

1,2,6-hexanetriol and its mono ester derivatives, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, 1,4-butanediol, and the like. These materials have many inherent disadvantages including excessive volatility, poor solvency in organic media, marginal co-reactivity, and marginal compatibility with the base film forming polymer. The lower molecular weight members are especially prone to cratering and other application defects while the higher members of the series do not adequately reduce the viscosity or provide sufficient co-reactivity with the base polymer and or cross-linking agent. Later polyols derived from alkylene oxides were used. Typical of these materials are polypropylene glycols, polyethylene glycol, and copolymers in the molecular weight range of 225 to 3000; these materials have improved non-volatile character but do not provide either good solvency for a variety of film forming polymers or acceptable exterior durability in the more demanding applications. Of special interest in this category are the polyether diols derived from bisphenol A and ethylene or propylene oxide. Still later, hydroxy terminated polyesters were introduced. These materials are low molecular weight polyesters of M.W. 300 to 3000 derived from caprolactone, cyclic diols, e.g., cyclohexane dimethanol and dibasic acids such as phthalic, isophthalic, maleic, succinic and the like. Often small quantities of triols or tetrols were used to create polyfunctionality in the polyester. These materials are in effect very low molecular weight

- 9 -

oil less alkyds. They are characterized by a broad compatibility, good co-reactivity, and low volatility. These materials represent an improvement over the polyether diols, however they provide neither the viscosity reduction for many applications methods including spray and electrostatic spray nor performance required for the more demanding end uses.

Today the state of the art has advanced to the point where the real needs are apparent and further improvement in high solids coatings systems will require more versatile reactive solvents and reactive diluents.

It is the objective of the present invention to demonstrate coating compositions which employ one or more nearly non-volatile, substituted carbamates to replace all or part of the volatile organic solvent or diluent used in high solids coating compositions. The substituted carbamates of the present invention have as an integral part of their structure a plurality of reactive -OH and/or -NHCO- groups which are capable, through the application of heat and/or in the presence of catalytic agents when required, of reacting with the base film forming polymers and cross-linking agents.

It is the further objective of this invention to provide reactive solvents/reactive diluents which serve to provide high solids coatings compositions in the form of either solutions or dispersions.

It is still another objective of this invention to provide reactive solvents and reactive

- 10 -

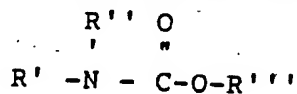
diluents which will not degrade the quality or performance of the final finished coating.

Other objects will become apparent to those skilled in the art upon a further reading of the specifications.

### Summary of the Invention

High solids coating compositions meeting the objects above can be prepared by blending;

- (a) at least one crosslinkable organic polymer free of amide groups;
- (b) organic solvent;
- (c) at least one reactive carbamate derivative having the generic formula:



wherein

each of R' and R'' is a monovalent radical selected from the group consisting of hydrogen, alkyl groups having 1 to about 10 carbons, hydroxyalkyl groups having 2 to about 4 carbon atoms, hydroxyalkyleneoxy groups and hydroxypolyalkyleneoxy groups and R''' is the same as R' or R'' except that it cannot be hydrogen, with the provisos that:

said hydroxyalkyl, hydroxyalkyleneoxy and hydroxypolyalkyleneoxy groups contain at least 1 OH group;

said R' and R'' or R' and R''' groups can unite to form a carbon ring structure; and

- 11 -

said carbamate derivatives contain either at least one -NH and one -OH group or at least two OH groups;

(d) a crosslinking amount of a crosslinking agent; and

(e) optionally a catalytic amount of a crosslinking catalyst.

In the above carbamate derivatives except for hydrogen, the monovalent radicals may be substituted with ether, halogen, quaternary ammonium, sulfonium, phosphonium and like substituents.

Suitable organic polymers for use in the present invention include polymers which contain a plurality of reactive -OH and/or -NHCOO -groups.

Preferred crosslinkable organic polymers for use in this invention having as an integral part of their structure a plurality of reactive -OH and/or -NH groups include:

Polyurethane resins

Polyester alkyd resins

Hydroxyl containing epoxy fatty acid esters

Hydroxyl containing polyesters

Hydroxyl containing alkyd resins

Hydroxyl containing acrylic interpolymers except acrylamides

Hydroxyl containing vinyl interpolymers, such as styrene/acrylic copolymers.

The ratio of the amounts of solvent and reactive diluent or cosolvent used to prepare the coating compositions is dictated by the type of coating desired. Thus in the dispersion type, the

- 12 -

amount of reactive diluent is usually determined by the film properties desired. Usually these can be attained by ratios of reactive diluent/solvent in the range of about 5/95 to about 30/70. On the other hand in the solution type the ratio of reactive cosolvent to solvent is limited by the solubility characteristics of the polymer. Thus a more soluble polymer would require less reactive cosolvent while a less soluble polymer would require more. Generally, polymers of these types are soluble in a blend of reactive cosolvent/solvent of about 20/80 to about 60/40. In practice the base coating may be formulated at rather high ratios of reactive cosolvent/solvent i.e., about 60/40 to about 90/10 and then let down with solvent to attain application viscosities. One skilled in the art can easily establish the optimum ratios for a particular coating composition with a minimum of experimentation. The amount of organic polymer used in these compositions is not narrowly critical. However, a practical range for the solution type is about 15 to about 45% by weight of polymer with the amount of reactive solvent being about 10 to about 20% by weight, the amount of crosslinker being about 10 to about 30% by weight and the amount of solvent being about 60 to about 5% by weight.

A practical range of organic polymer used for the dispersion type of coating composition is about 35 to about 50% by weight, with the amount of reactive diluent being about 5 to about 20% by weight, the amount of crosslinker being about 5 to

- 13 -

about 20% by weight and the amount of solvent being about 55 to about 10% by weight.

The reactive carbamate derivatives in the coating composition claimed herein can be designated as either reactive cosolvents or reactive diluents depending on the type of coatings formed. In the case of coating compositions which are dispersions, the carbamates function as reactive diluents. In the case of coating compositions which are solutions, the carbamates function as reactive cosolvents.

The term reactive is used herein to mean that the carbamate derivatives can be incorporated into the finished coating by crosslinking agents which cure through NH and/or OH groups.

The reactive carbamates used in this invention may be represented by the following:

- butyl 6-hydroxyhexylcarbamate
- 2-ethylhexyl 4-hydroxybutylcarbamate
- butyl 2-hydroxyethylcarbamate
- 2-ethylhexyl 2,3-dihydroxy-1-propylcarbamate
- butyl 2,3-dihydroxy-1-propylcarbamate
- hexyl bis-(2-hydroxyethyl)carbamate
- 2-(2-hydroxyethoxy) ethyl carbamate
- 4-hydroxybutyl carbamate
- 2-hydroxy-1-propyl carbamate
- 1-hydroxy-2-propyl carbamate
- 2-hydroxyethyl carbamate
- 1,3-dihydroxy-2-propyl carbamate
- 2,3-dihydroxy-1-propyl carbamate
- 2-hydroxydecyl carbamate
- 1-(hydroxymethyl)nonyl carbamate

- 14 -

2-hydroxyethyl (2-hydroxyethyl)-  
(ethyl)carbamate

1,3-dihydroxy-2-propyl dimethylcarbamate

2,3-dihydroxy-1-propyl dimethylcarbamate

2,3-dihydroxy-1-propyl tetramethylene-  
carbamate

2-hydroxyethyl bis-(2-hydroxyethyl)carbamate

3-(2,3-dihydroxy-1-propyl) oxazolidone

2-hydroxyethyl dimethyl carbamate

3-(2-hydroxyethyl)-5-(hydroxymethylene)-  
oxazolidone

3-(2-hydroxyethyl) oxazolidone

2-hydroxyethyl 1-butylcarbamate

1-hydroxy-2-propyl 1-propylcarbamate

2-hydroxy-1-propyl 1-propylcarbamate

1-hydroxy-2-propyl 1-butylcarbamate

2-hydroxy-1-propyl 1-butylcarbamate

2-methyl-1-propyl 2-hydroxyethylcarbamate

2-propyl bis(2-hydroxyethyl)carbamate

2-hydroxyethyl methylcarbamate

2-hydroxyethyl 2-hydroxyethylcarbamate

2,3-dihydroxy-1-propyl ethylcarbamate

1,3-dihydroxy-2-propyl 1-butylcarbamate

5-(hydroxymethylene) oxazolidone

4-(hydroxymethylene) oxazolidone

1,3-dihydroxy-2-propyl ethylcarbamate

2-hydroxyethyl ethylcarbamate

2-hydroxyethyl 2-methylpropylcarbamate

2-hydroxy-1-propyl 2-ethylhexylcarbamate

2,3-dihydroxy-1-propyl 1-butylcarbamate

1-hydroxy-2-propyl 2-ethylhexylcarbamate

5-(hydroxymethylene)oxazolidone



- 15 -

1,3-dihydroxy-2-propyl tetramethylene  
carbamate  
5-hydroxypyrazolidone  
2-hydroxyethyl  
(propyl)(2-hydroxyethyl)carbamate  
2-hydroxy-1-propyl 2-hydroxyethylcarbamate  
2-hydroxyethyl 3-hydroxy-2,2-dimethyl-1-  
propylcarbamate

Illustrative of suitable crosslinking agents for the high solids coating compositions described herein are methylol phenols, such as 2,4,6-trimethylolphenol, polyepoxides, such as the glycidyl epoxides or cycloaliphatic epoxides (Araldite\* 297, Epon\* 582, etc.) and the aminoplasts such as the reaction product of an aldehyde (e.g. formaldehyde, acetaldehyde, paraformaldehyde, trioxane, etc.) with urea, thiourea, melamine, benzoguanamine, acetoguanamine, dicyandiamine and the like. The aminoplasts may be etherified with a lower alcohol such as methyl, ethyl, butyl, isobutyl, propyl or isopropyl alcohol. Aminoplasts which are of particular value in high solids coating compositions are the methylated urea-formaldehyde resins, the alkylated benzoguanamines and methylated melamine-formaldehyde resins with the latter being the most desirable.

However the crosslinking agent is not an aminoplast unless there are two or more or no OH groups on the R''' moiety or unless R' and R'' are each hydrogen or neither R' nor R'' is hydrogen.

The choice of catalysts suitable for the practice of this invention is dictated by the choice

- 16 -

of crosslinking reaction. Thus if aminoplasts are employed to crosslink the organic polymer and reactive carbamate, an acidic catalyst is preferred. Illustrative of the acidic catalyst of the invention are one or more of the following: alkylsulfonic acids such as methane sulfonic acid, ethane sulfonic acid and the like, arylsulfonic acids such as p-toluene sulfonic acid, alkylaryl sulfonic acids such as a C<sub>10</sub> to C<sub>18</sub> alkylbenzene sulfonic acid, dialkyl hydrogen phosphates such as diamyl hydrogen phosphate, aryl hydrogen phosphates such as diphenyl hydrogen phosphate and phosphoric acid itself.

The diisocyanates and blocked diisocyanates are often employed to crosslink these polymers. The polymer isocyanates have been extensively reviewed by Wicks (Prog. Org. Chem. 3, 73 (1975)). A blocked isocyanate is an isocyanate adduct which is stable at ambient conditions but dissociates to regenerate isocyanate functionality under the influence of heat. Temperatures of 120 to about 250°C are necessary to release the blocking groups which are usually volatilized from the coating. The dissociation temperature of blocked isocyanates based on commercially utilized blocking agents decrease in the order: epsilon-caprolactam, phenols, methyl ethyl ketoxime, and active methylene compounds. Blocked isocyanates which are stable have been described by Rosthauser and Williams (Proceedings Polymeric Materials Science and Engineering; Vol. 50, pg. 344 (1984)). Catalysts which promote the urethane reaction are well known

- 17 -

to the art and are illustrated by tertiary amines such as triethyl amine, bis(dimethylaminoethyl) ether and the like, organometallic salts of tin, mercury, zinc, bismuth and the like such as dibutyl tin diacetate, zinc octoate, phenyl mercuric acetate and bismuth octoate.

The amount of catalyst required to promote the reaction is dependent upon the curing conditions required in the coating process. Those skilled in the art may readily determine the catalyst level with a minimum of experimentation. In practice if a catalyst is desired it is usually in the level of .02 to about 1% based on the weight of the organic polymer.

Background of the curing relations of hexamethoxymethylmelamine may be found in an article by R. Saxon et al. in J. Appl. Poly. Sci. 8, 475 (1964).

The invention is further described in the examples which follow. All parts and percentages are by weight unless otherwise specified.

#### Example 1

##### PREPARATION OF 2-HYDROXYETHYL DIMETHYLCARBAMATE

When ethylene carbonate is treated as in U.S. 4,520,167 with an equimolar amount of dimethylamine, a mixture containing 2-hydroxyethyl dimethylcarbamate is obtained.

#### Example 2

##### PREPARATION OF 3-(2-HYDROXYETHYL) OXAZOLIDONE

When dimethyl carbonate is treated with an equimolar amount of diethanolamine, a mixture containing 3-(2-hydroxyethyl)oxazolidone is obtained.

- 18 -

Example 3PREPARATION OF 2-HYDROXYETHYL  
(2-HYDROXYETHYL) (ETHYL) CARBAMATE

When ethylene carbonate is treated as in Example 1 with an equimolar amount of N-ethyl ethanolamine, a mixture containing 2-hydroxyethyl (2-hydroxyethyl) (ethyl) carbamate is obtained.

Example 43-(2-HYDROXYETHYL) OXAZOLIDONE/CARGILL-7451\*  
RESIN CROSSLINKED BY CYMEL-323

When 3-(2-hydroxyethyl)oxazolidone is combined with CELLOSOLVE\* Acetate Solvent, Cargill\*-7451 resin, CYMEL\*-303 crosslinker (in an amount stoichiometrically equivalent to the sum of resin and oxazolidone) and p-toluenesulfonic acid catalyst, a mixture is obtained which can be thermally cured into a hard, tough, glossy coating.

Example 52-HYDROXYETHYL (2-HYDROXYETHYL) (ETHYL)  
CARBAMATE/CARGILL\*-7451 RESIN  
CROSSLINKED BY CYMEL\* 303

When Example 4 is repeated with the exception that 2-hydroxyethyl(2-hydroxyethyl) (ethyl) carbamate is substituted for 3-(2-hydroxyethyl) oxazolidone, a mixture is obtained which can be thermally cured into a tough, hard, glossy coating.

- 19 -

Example 6PREPARATION OF  
1,3-DIHYDROXY-2-PROPYL CARBAMATE AND  
2,3-DIHYDROXY-1-PROPYL CARBAMATE

When glycerine is treated with dimethylcarbonate, a mixture is obtained which contains cyclic carbonates of glycerine (4-hydroxymethyl-1,3-dioxol-2-one and 5-hydroxy-1,3-dioxan-2-one). When the mixture containing these cyclic carbonates is treated with ammonia, another mixture is obtained which contains 1,3-dihydroxy-2-propyl carbamate and 2,3-dihydroxy-1-propyl carbamate.

Example 7PREPARATION OF  
1,3-DIHYDROXY-2-PROPYL TETRAMETHYLENE CARBAMATE  
AND 2,3-DIHYDROXY-1-PROPYL TETRAMETHYLENE CARBAMATE

When Example 6 is followed except that the ammonia is replaced by pyrrolidine, a mixture is obtained which contains 1,3-dihydroxy-2-propyl tetramethylene carbamate and 2,3-dihydroxy-1-propyl tetramethylenecarbamate.

Example 81,3 DIHYDROXY-2-PROPYL TETRAMETHYLENE CARBAMATE AND  
2,3-DIHYDROXY-1-PROPYL TETRAMETHYLENE CARBAMATE AND  
CARGILL\* 7451 RESIN CROSSLINKED BY CYMEL\* 303

A mixture containing 1,3-dihydroxy-2-propyl tetramethylenecarbamate, 2,3-dihydroxy-1-propyl tetramethylenecarbamate, CELLOSOLVE Acetate Solvent, CARGILL-7451 resin, CYMEL-303 crosslinker and p-toluenesulfonic acid catalyst is thermally cured to give a hard, tough glossy coating.

- 20 -

Example 9PREPARATION OF HYDROXYETHYL BUTYLCARBAMATE

274.8 Grams of ethylene carbonate (3.12 moles) were placed in a round bottom flask equipped with stirrer, thermometer, addition funnel and reflux condenser. 228.2 Grams (3.12 mole) of butylamine were charged to the addition funnel and added to the stirred contents of the flask at a rate sufficient to maintain them at 50-80°C. Crude product purity by gas chromatography was 90.6 area % after the mixture had been allowed to stand overnight. Stripping in a rotary evaporator gave 449.9 g. of product of 92.3 area % purity. The yield, corrected for purity, was 83.1%. A portion of the material was distilled at 2 mm Hg boiling from 124 to 126°C and having area % purity 95.1%.

Hydroxyethyl butylcarbamate is a good solvent for a polyester resin (Cargill #7451).

Example 10PREPARATION OF 2-HYDROXYETHYL METHYLCARBAMATE

44 Grams (.5 mole) of ethylene carbonate were placed in a 250-ml round bottom flask equipped with stirrer, addition funnel, and thermometer. 38.75 Grams of 40% aqueous methylamine (15.5 g., .5 mole contained methylamine) were charged to the addition funnel and added to the flask with stirring over 1.25 hr. and with the flask contents at 38 to 52°C. The resulting mixture was subjected to vacuum distillation giving 42.54 g. (35.7%) of clear, colorless liquid product boiling at 140°C at 8 mm Hg. The infrared spectrum of this material was consistent with the proposed structure. Purity by

- 21 -

gas chromatography was 97.8 area %. The product had a melting point of approximately -36°C and was miscible with water.

Example 11

PREPARATION OF HYDROXYPROPYL BUTYLCARBAMATES

290.96 grams (2.85 moles) of propylene carbonate were charged to a 2-l, round bottom flask equipped with stirrer, heater, thermometer, addition funnel and reflux condenser. 211.3 Grams (2.85 moles) of butylamine were charged to the addition funnel and slowly added to the flask contents. The maximum temperature of the reaction was 98°C. The material was allowed to stand and a sample submitted for infrared analysis. The infrared spectrum was consistent with the proposed structures (i.e. an isomeric mixture of 2-hydroxy-1 and 1-hydroxy-2-propyl 1-butylcarbamates). The proposed structures given above were confirmed by Proton NMR analysis.

Example 12

HYDROXYETHYL BUTYLCARBAMATE/CARGILL\*-7451 RESIN  
CROSSLINKED BY A BLOCKED AROMATIC ISOCYANATE  
PREPOLYMER BASED ON TOLUENE DIISOCYANATE

A mixture of hydroxyethyl butylcarbamate, Cargill\*-7451 Resin, CELLOSOLVE\* Acetate and a blocked aromatic isocyanate prepolymer based on toluene diisocyanate (as taught in U.S. 4,518,522 assigned to Mobay) is thermally cured to a hard, tough glossy coating.

- 22 -

Example 13HYDROXYETHYLBUTYL CARBAMATE AND CARGILL\* 7451  
RESIN CROSSLINKED BY EPON\*828

A mixture of hydroxyethyl butylcarbamate, Cargill\* -7451 resin, CELLOSOLVE\* Acetate, EPON\* -828 and an amine catalyst is thermally cured to afford a hard, tough, glossy coating.

Example 14PREPARATION OF HYDROXYPROPYL PROPYLCARBAMATES

722 Grams (7.0 moles @ 99% purity) of propylene carbonate was charged to a 2 l round-bottom flask equipped with stirrer, heating mantle thermometer, feed tank and distillation head. The flask and contents were heated with stirring under nitrogen to 50°C. At this point addition of 436 grams (7 moles @ 98% purity) of n-propylamine was begun and continued for a total of 3.25 hrs. during which time the temperature was maintained between 50 and 62°C without external heat. The temperature was then raised to 72°C and held at this value for an additional 3 hrs. then the flask and contents were allowed to cool and stand overnight. Lights were removed by heating to a maximum temperature of 105°C under 2 mm Hg pressure during 1 hr. with stirring.

Gas chromatographic analysis of this material showed 96.8 area % product.



- 23 -

Example 15SYNTHESIS OF 2-HYDROXYETHYL 2-ETHYLHEXYLCARBAMATE

When Example 9 is followed except that a chemically equivalent amount of 2-ethylhexyl amine is substituted for n-butylamine, a mixture containing 2-hydroxyethyl 2-ethylhexylcarbamate is obtained.

Example 16SYNTHESIS OF HYDROXYPROPYL 2-ETHYLHEXYLCARBAMATES

When Example 14 is followed except that a chemically equivalent amount of 2-ethylhexylamine is substituted for n-propylamine, an isomeric mixture of 2-hydroxy-1-propyl 2-ethylhexylcarbamate and 1-hydroxy-2-propyl 2-ethylhexylcarbamate is obtained.

Example 17PREPARATION OF 2-METHYL-1-PROPYL  
(2-HYDROXYETHYL)CARBAMATE

An equimolar mixture of di(2-methyl-1-propyl)carbonate and ethanolamine is allowed to react resulting in formation of a mixture containing 2-methyl-1-propyl (2-hydroxyethyl)carbamate.

Example 18SYNTHESIS OF 2-HYDROXYETHYL  
(2-HYDROXYETHYL)CARBAMATE

When example 9 is followed except that a chemically equivalent amount of ethanolamine is substituted for n-butylamine, a mixture containing 2-hydroxyethyl (2-hydroxyethyl)carbamate is obtained.

- 24 -

Example 19SYNTHESIS OF BUTYL  
2,3-DIHYDROXYPROPYLCARBAMATE

An equimolar mixture of dibutylcarbonate and 3-amino-1,2-propanediol is allowed to react resulting in formation of a mixture containing butyl 2,3-dihydroxypropylcarbamate.

Example 201-HYDROXY-2-PROPYL 1- BUTYL CARBAMATE  
2-HYDROXY-1- PROPYL 1-BUTYL CARBAMATE,  
CARGILL\* 7451 RESIN CROSSLINKED BY A  
BLOCKED AROMATIC ISOCYANATE PREPOLYMER

When example 12 is followed excepting that a chemically equivalent amount of an isomeric mixture of 1-hydroxy-2-propyl 1-butylcarbamate and 2-hydroxy-1-propyl 1-butyl carbamate is substituted for hydroxyethyl butylcarbamate, a mixture is obtained which can be thermally cured to a hard, tough, glossy coating.

Example 211-HYDROXY-2-PROPYL 1-PROPYLCARBAMATE, 2-HYDROXY-1-  
PROPYL 1-PROPYLCARBAMATE, CARGILL\* 7451  
RESIN CROSSLINKED BY A BLOCKED AROMATIC ISOCYANATE  
PREPOLYMER BASED ON TOLUENE DIISOCYANATE.

When Example 12 is followed except that a chemically equivalent amount of an isomeric mixture of 1-hydroxy-2-propyl 1-propylcarbamate and 2-hydroxyl-1-propyl 1-propylcarbamate is substituted for 2-hydroxyethyl 1-butylcarbamate, a hard, glossy, tough coating is obtained.

- 25 -

Example 22PREPARATION OF 5-(HYDROXYMETHYLENE)OXAZOLIDONE  
AND 5-HYDROXYPYRAZOLIDONE

An equimolar mixture of dimethyl carbonate and 3-amino-1,2-propanediol is allowed to react resulting in a mixture containing 5-(hydroxymethylene) oxazolidone and 5-hydroxypyrazolidone.

Example 23PREPARATION OF 2-HYDROXYETHYL 3-HYDROXY-  
2,2-DIMETHYL-1-PROPYLCARBAMATE.

An equimolar mixture of ethylene carbonate and 3-amino-2,2-dimethyl-1-propanol is allowed to react resulting in a mixture containing 2-hydroxyethyl 3-hydroxy-2,2-dimethyl-1-propylcarbamate.

Example 24PREPARATION OF 2-HYDROXYETHYL (PROPYL)  
(2-HYDROXYETHYL)CARBAMATE

When Example 9 is followed except that the butylamine is replaced by an equimolar amount of N-propyl ethanolamine, a mixture is obtained which contains 2-hydroxyethyl (propyl)(2-hydroxyethyl)-carbamate.

Example 25PREPARATION OF 2-HYDROXYETHYL CARBAMATE

When ethylene carbonate (1,3-dioxol-2-one) is treated with ammonia a mixture is obtained which contains 2-hydroxyethyl carbamate.

- 26 -

Example 26PREPARATION OF 2-(2-HYDROXYETHOXY)ETHYL CARBAMATE

When urea is treated with diethylene glycol (2-(2-hydroxyethoxy) ethanol), a mixture is obtained which contains 2-(2-hydroxyethoxy)ethyl carbamate.

Example 27PREPARATION OF 4-HYDROXYBUTYL CARBAMATE

When urea is treated with 1,4 butanediol, a mixture is obtained which contains 4-hydroxybutyl carbamate.

Example 28PREPARATION OF A MIXTURE OF 2-HYDROXYDECYL CARBAMATE AND 1-(HYDROXYMETHYL)NONYL CARBAMATE

When urea is treated with 1,2-decanediol, a mixture is obtained which contains 2-hydroxydecyl carbamate and 1-(hydroxymethyl) nonyl carbamate.

Example 292-HYDROXYDECYL CARBAMATE,  
1-(HYDROXY-METHYL)NONYL CARBAMATE AND  
CARGILL-7451 RESIN CROSSLINKED BY CYMEL-303

A mixture of 2-hydroxydecyl carbamate, 1-(hydroxymethyl)nonyl carbamate, CELLOSOLVE\* Acetate, Cargill-7451 Resin, Cymel\*-303-crosslinker and p-toluenesulfonic acid is thermally cured to give a hard, tough, glossy coating.

Example 30PREPARATION OF BUTYL 2-HYDROXYETHYL CARBAMATE

When dibutylcarbonate is treated with 2-aminoethanol a mixture is obtained which contains butyl 2-hydroxyethylcarbamate.

- 27 -

Example 31PREPARATION OF 2-ETHYLHEXYL 4-HYDROXYBUTYLCARBAMATE

When di(2-ethylhexyl)carbonate is treated with 4-amino-1-butanol, a mixture is obtained which contains 2-ethylhexyl 4-hydroxybutylcarbamate.

Example 32PREPARATION OF BUTYL 6-HYDROXYHEXYLCARBAMATE

When dibutylcarbonate is treated with 6-amino-1-hexanol a mixture is obtained which contains butyl 6-hydroxy hexylcarbamate.

Example 33BUTYL 6-HYDROXYHEXYLCARBAMATE AND  
CARGILL\*-7451 RESIN CROSSLINKED BY  
CYMEL-327

A mixture containing butyl 6-hydroxyhexylcarbamate, CELLOSOLVE Acetate Solvent, Cargill-7451 resin and Cymel-327 crosslinker is thermally cured to give a hard, tough, glossy coating.

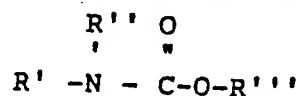
Although the invention has been described in its preferred forms with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example and that numerous changes can be made without departing from the spirit and the scope of the invention.

- 28 -

CLAIMS

1. Method of making solvent borne high solids coating compositions which comprises blending:

- (a) at least one crosslinkable organic polymer free of amide groups;
- (b) organic solvent;
- (c) at least one reactive carbamate derivative having the generic formula:



wherein

each of R' and R'' is a monovalent radical selected from the group consisting of hydrogen, alkyl groups having 1 to 10 carbons, hydroxyalkyl groups having 2 to about 4 carbon atoms, hydroxyalkyleneoxy groups and hydroxypolyalkyleneoxy groups and R''' is the same as R' or R'' except that it cannot be hydrogen, with the provisos that:

said hydroxyalkyl, hydroxyalkyleneoxy and hydroxypolyalkyleneoxy groups contain at least 1 OH group;

said R' and R'' or R' and R''' groups can unite to form a carbon ring structure; and

said carbamate derivatives contain either at least one -NH and one -OH group or at least two OH groups;

(d) a crosslinking amount of a crosslinking agent; and

(e) optionally a catalytic amount of a crosslinking catalyst.

- 29 -

2. Method claimed in claim 1 wherein R' and R'' are each methyl and R''' is 1,3-dihydroxy-2-propyl.

3. Method claimed in claim 1 wherein R' is ethyl and R'' and R''' are each hydroxyethyl.

4. Method claimed in claim 1 wherein R' and R'' are each methyl and R''' is 2,3-dihydroxy-1-propyl.

5. Method claimed in claim 1 wherein R' and R'' are linked to form a carbon ring structure and R''' is 2,3-dihydroxy-1-propyl.

6. Method claimed in claim 1 wherein R' and R'' are linked to form a tetramethylene chain and R''' is 2,3-dihydroxy-1-propyl.

7. Method claimed in claim 1 wherein R' is hydrogen, R'' is 6-hydroxyhexyl and R''' is butyl.

8. Method claimed in claim 1 wherein R''' is 2-hydroxyethyl and R' and R'' are each hydrogen.

9. Method claimed in claim 1 wherein R''' is 4-hydroxybutyl and R' and R'' are each hydrogen.

10. Method claimed in claim 1 wherein R''' is 1-hydroxy-2-propyl and R' and R'' are each hydrogen.

11. Method claimed in claim 1 wherein R''' is 2-hydroxy-1-propyl and R' and R'' are each hydrogen.

- 30 -

12. Method claimed in claim 1 wherein R''' is 2-hydroxydecyl and R' and R'' are each hydrogen.

13. Method claimed in claim 1 wherein R''' is 1-(hydroxymethyl)nonyl and R' and R'' are each hydrogen.

14. Method claimed in claim 1 wherein R' is hydrogen, R'' is methyl and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

15. Method claimed in claim 1 wherein R' is hydrogen, R'' is butyl and R''' is hydroxybutyl wherein the crosslinking agent is one other than an aminoplast.

16. Method claimed in claim 1 wherein R' is hydrogen, R'' is butyl and R''' is hydroxypropyl wherein the crosslinking agent is one other than an aminoplast.

17. Method claimed in claim 1 wherein R' is hydrogen, R'' is 2-ethylhexyl and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

18. Method claimed in claim 1 wherein R' is hydrogen, R'' is isobutyl and R''' is 2-hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

19. Method claimed in claim 1 wherein R' is n-propyl and R'' and R''' are each hydroxyethyl.



- 31 -

20. Method claimed in claim 1 wherein R' is hydrogen and R'' and R''' are each hydroxyethyl.

21. Method claimed in claim 1 wherein R' is hydrogen, R'' is hydroxyethyl and R''' is 2-hydroxy-1-propyl.

22. Method claimed in claim 1 wherein R' and R'' are each methyl and R''' is 1,3-dihydroxy-2-propyl.

23. Method claimed in claim 1 wherein the organic polymer is a hydroxyl containing polyester alkyd resin.

24. Method claimed in claim 1 wherein the organic polymer is a hydroxy containing epoxy fatty acid ester.

25. Method claimed in claim 1 wherein the organic polymer is a hydroxy containing polyester.

26. Method claimed in claim 1 wherein the organic polymer is a hydroxy containing alkyd resin.

27. Method claimed in claim 1 wherein the organic polymer is a hydroxy containing acrylic interpolymer.

28. Method claimed in claim 27 wherein the organic polymer is a homogeneously dispersed, hydroxyl containing acrylic interpolymer.

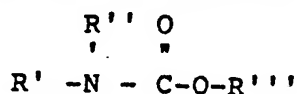
29. Coating composition made by the method claimed in claim 1.

- 32 -

30. Method of coating substrates with organic polymers which comprises:

(1) contacting said substrates with a coating composition prepared by blending:

- (A) at least one crosslinkable organic polymer free of amide groups;
- (B) organic solvent;
- (C) at least one reactive carbamate derivative having the generic formula:



wherein

each of R' and R'' is a monovalent radical selected from the group consisting of hydrogen, alkyl groups having 1 to about 10 carbons, hydroxyalkyl groups having 2 to about 4 carbon atoms, hydroxyalkyleneoxy groups and hydroxypolyalkyleneoxy groups and R''' is the same as R' or R'' except that it cannot be hydrogen, with the provisos that:

said hydroxyalkyl, hydroxyalkyleneoxy and hydroxypolyalkyleneoxy groups contain at least 1 OH group;

said R' and R'' or R' and R''' groups can unite to form a carbon ring structure; and

said carbamate derivatives contain either at least one -NH and one -OH group or at least two OH groups;

(D) a crosslinking amount of a crosslinking agent; and

(E) optionally a catalytic amount of a crosslinking catalyst, and

(2) curing said coating composition.

- 33 -

31. Method claimed in claim 30 wherein R' is hydrogen, R'' is methyl and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

32. Method claimed in claim 30 wherein R' is hydrogen, R'' is butyl and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

33. Method claimed in claim 30 wherein R' is hydrogen, R'' is butyl and R''' is hydroxypropyl wherein the crosslinking agent is one other than an aminoplast.

34. Method claimed in claim 30 wherein R' is ethyl, R'' is hydrogen and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

35. Method claimed in claim 30 wherein R' is hydrogen, and R'' is isobutyl and R''' is hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

36. Method claimed in claim 30 wherein R' is propyl, R'' and R''' are each hydroxyethyl.

37. Method claimed in claim 30 wherein R' is hydrogen, R'' and R''' are each hydroxyethyl wherein the crosslinking agent is one other than an aminoplast.

- 34 -

38. Method claimed in claim 30 wherein R''' is hydroxyethyl and R' and R'' are each hydrogen.

39. Method claimed in claim 30 wherein R''' is 4-hydroxybutyl and R' and R'' are each hydrogen.

40. Method claimed in claim 30 wherein R''' is 1-hydroxy-2-propyl and R' and R'' are each hydrogen.

41. Method claimed in claim 30 wherein R''' is 2-hydroxy-1-propyl and R' and R'' are each hydrogen.

42. Method claimed in claim 30 wherein R''' is 1-(hydroxymethyl)nonyl and R' and R'' are each hydrogen.

43. Method claimed in claim 30 wherein R' and R'' are each methyl and R''' is 2,3-dihydroxy-1-propyl.

44. Method claimed in claim 30 wherein R' and R'' are linked to form a tetramethylene chain and R''' is 2,3-dihydroxy-1-propyl.

45. Method claimed in claim 30 wherein R' is hydrogen, R'' is 2-hydroxyethyl and R''' is butyl.

46. Method claimed in claim 30 wherein R' is hydrogen, R'' is 6-hydroxyhexyl and R''' is butyl.

- 35 -

47. Method claimed in claim 30 wherein the crosslinking agent is hexamethoxymethylmelamine.

48. Method claimed in claim 47 wherein the crosslinking catalyst is p-toluenesulfonic acid.

49. Method claimed in claim 30 wherein the organic polymer is a hydroxyl containing polyester alkyd resin.

50. Method claimed in claim 30 wherein the organic polymer is a hydroxyl containing epoxy fatty acid ester.

51. Method claimed in claim 30 wherein the organic polymer is a hydroxyl containing polyester.

52. Method claimed in claim 30 wherein the organic polymer is a hydroxyl containing acrylic interpolymer free of amide groups.

53. Method claimed in claim 52 wherein the organic polymer is a homogeneously dispersed, hydroxyl containing acrylic interpolymer free of amide groups.

54. Method claimed in claim 1 wherein the crosslinking agent is one other than an aminoplast.

55. Method claimed in claim 30 wherein the crosslinking agent is one other than an aminoplast.

56. Method claimed in claim 1 wherein the crosslinking agent is a blocked aromatic isocyanate prepolymer based on toluene diisocyanate.

## DIAGRAM OF HIGH SOLIDS DISPERSION COATING

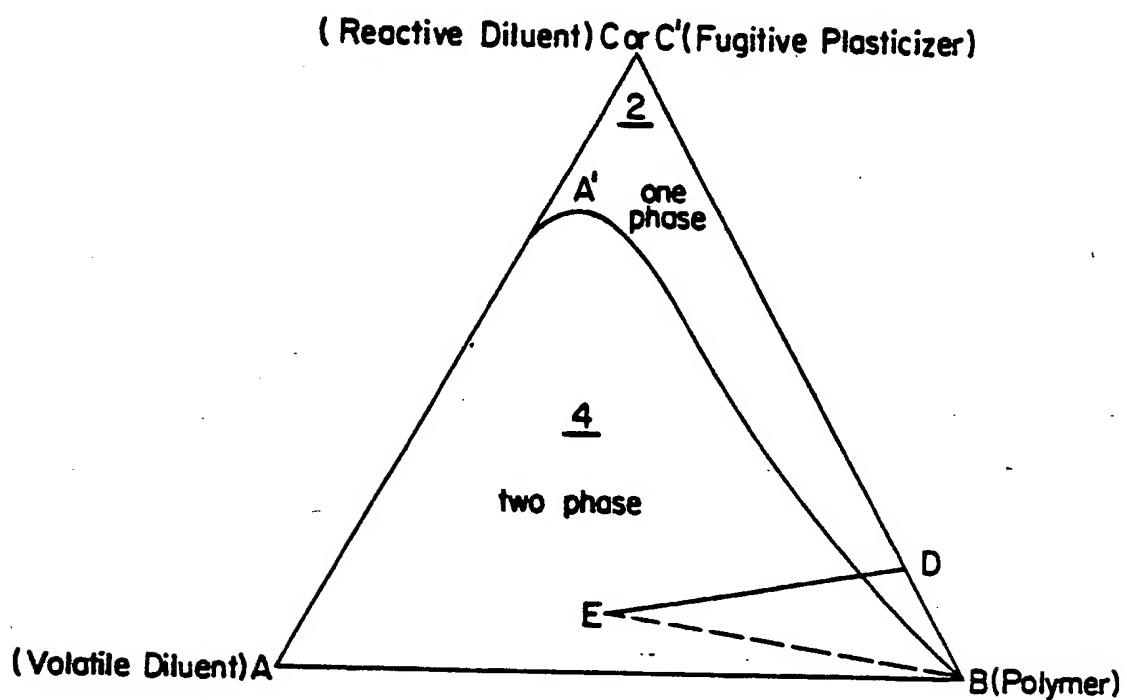
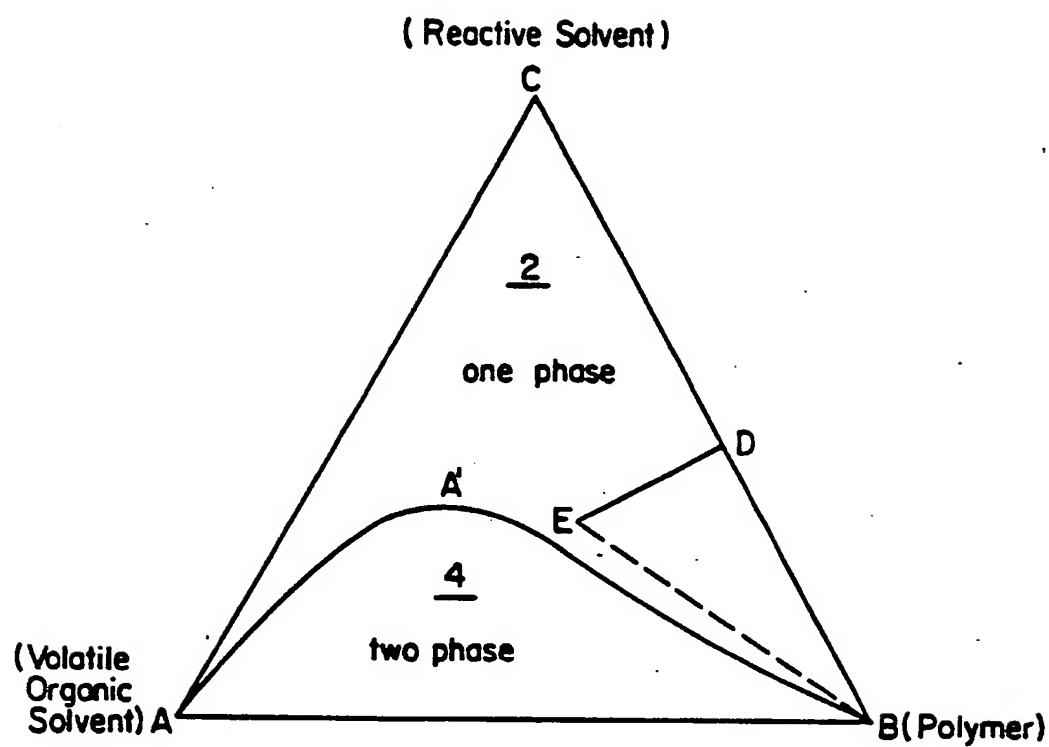


FIG. 1

# PHASE DIAGRAM OF HIGH SOLIDS SOLUTION COATING



## FIG. 2

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/01611

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>4</sup>: C 09 D 7/12

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System

Classification Symbols

IPC<sup>4</sup>: C 09 D

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4520167 (WERNER J. BLANK) 28 May 1985 see the abstract; claims 1,7,8,14; column 7, line 14; column 7, table I	1,14,16-18,20, 23,25-30,31- 35,37,47-49, 51-53

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

5th November 1986

Date of Mailing of this International Search Report

14 JAN. 1987

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. VAN MCL



ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/01611 (SA 14226)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/11/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4520167	28/05/85	EP-A- 0152820	28/08/85
		AU-A- 3876385	22/08/85

For more details about this annex :  
see Official Journal of the European Patent Office, No. 12/82

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